

# PATENT SPECIFICATION

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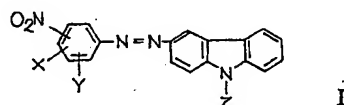


## (54) WATER-INSOLUBLE MONOAZO DYESTUFFS

(71) We, CASSELLA FARBWERKE  
 MAINKUR AKTIENGESellschaft, a  
 body corporate organised under the laws of  
 Germany, of 6 Frankfurt (Main)-Fechenheim,  
 Germany, do hereby declare the invention,  
 for which we pray that a patent may be  
 granted to us, and the method by which it is  
 to be performed, to be particularly described  
 in and by the following statements:—

The present invention is concerned with  
 water-insoluble monoazo dyestuffs and a pro-  
 cess for their manufacture.

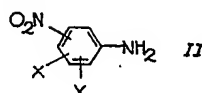
The monoazo dyestuffs of the present in-  
 vention are free of ionic groups and are of the  
 formula:



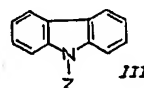
wherein X and Y are each hydrogen; halo-  
 gen; cyano; nitro or alkyl, alkylsulfonyl or  
 alkoxy having 1 to 6 carbon atoms and Z  
 is hydrogen; alkyl or alkenyl having 1 to 6  
 carbon atoms; said alkyl or said alkenyl sub-  
 stituted by cyano, hydroxy, acetoxy, alkoxy  
 having 1 to 4 carbon atoms, phenoxy, phenoxy-  
 acetoxy, monoalkylamino having 1 to 4 carbon  
 atoms or dialkylamino having 1 to 4 carbon  
 atoms in each alkyl moiety; phenalkyl having  
 1 to 2 carbon atoms in the alkyl moiety; cyclo-  
 alkyl having 3 to 6 carbon atoms; phenyl or  
 phenyl substituted by cyano or alkyl or alkoxy  
 having 1 to 4 carbon atoms.

The preferred cycloalkyl moieties for Z  
 include cyclopentyl and cyclohexyl. The cyclo-  
 alkyl radicals may be substituted with, for  
 example, cyano or alkyl or alkoxy having 1 to  
 4 carbon atoms. When X and Y are halogen,  
 they are preferably chlorine or bromine.

The dyestuffs of the present invention may  
 be obtained by diazotizing an amine of the  
 formula:



and coupling the resulting product with a car-  
 bazole of the formula:



X, Y and Z in the foregoing formulae having  
 the meanings set forth above.

It is also possible to diazotize mixtures of  
 two or more amines of formula II and to  
 couple the resulting product with a carbazole  
 derivative of formula III or a mixture of two  
 or more such carbazole derivatives. The result-  
 ing product is a mixture of the dyestuffs of  
 formula I and in certain instances has particu-  
 larly advantageous properties.

Suitable amines of formula II, include, for  
 example:

- 2-, 3- or 4 - nitroaniline
- 2 - nitro - 4 - or 6 - methylaniline
- 2 - nitro - 4,6 - dimethylaniline
- 2 - nitro - 4 - methoxy- or 4 - ethoxyaniline
- 2 - nitro - 4 - chloro- or 4 - bromoaniline
- 2 - nitro - 4 - methylsulfonyl- or 4 - n - hexyl-  
 sulfonylaniline
- 3 - nitro - 4 - methoxy- or 4 - ethoxyaniline
- 3 - nitro - 6 - methoxy- or 6 - ethoxyaniline
- 3 - nitro - 4 - cyanoaniline
- 2 - methyl-, 2 - ethyl- or 2 - isopropyl - 4 -  
 nitroaniline
- 2 - methoxy-, 2 - ethoxy- or 2 - n - butoxy-  
 4 - nitroaniline
- 3 - methoxy - 4 - nitroaniline
- 2,5 - dimethoxy- or 2,5 - diethoxy - 4 - nitro-  
 aniline
- 2 - chloro- or 2 - bromo - 4 - nitroaniline

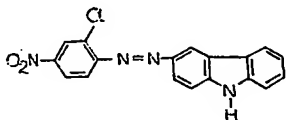
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- 2 - cyano - 4 - nitroaniline  
 2,6 - dichloro- or 2,6 - dibromo - 4 - nitro-  
 aniline  
 2 - chloro - 6 - bromo - 4 - nitroaniline  
 5 2 - cyano - 4 - nitro - 6 - chloro- or 6 - bromo-  
 aniline  
 2 - methylsulfonyl - 4 - nitroaniline  
 2 - methylsulfonyl - 4 - nitro - 6 - chloro- or  
 6 - bromoaniline  
 10 2,4 - dinitroaniline  
 2,4 - dinitro - 6 - chloro- or 6 - bromoaniline  
 2,4 - dibromo - 6 - cyanoaniline  
 2,4,6 - trinitroaniline

- Suitable coupling components of formula III  
 15 include those wherein Z is hydrogen, methyl,  
 ethyl, propyl, isopropyl, vinyl,  $\alpha$  - methyl-  
 vinyl, allyl, butyl, isobutyl, sec. - butyl, amyl,  
 isoamyl, hexyl, 2 - dimethylaminoethyl, 2-  
 diethylaminoethyl, 2 - cyanoethyl, 2 - hydroxy-  
 20 ethyl, 2 - acetoxyethyl, 2 - phenoxyacetoxy-  
 ethyl, 1 - methyl - 2 - hydroxyethyl, 3-  
 hydroxypropyl, 2 - methoxyethyl, 2 - ethoxy-  
 ethyl, 2 - phenoxyethyl, 3 - methoxypropyl,  
 cyclohexyl, benzyl, 3 - methylbenzyl, phenyl,  
 25 2 - methylphenyl, 4 - methylphenyl, 2,4 - di-  
 methylphenyl, 4 - cyanophenyl, 2 - methoxy-  
 phenyl or 4 - methoxyphenyl.

- The dyestuffs of the present invention are  
 particularly suitable for dyeing and printing  
 30 synthetic hydrophobic materials such as poly-  
 olefins, polyvinyl compounds, polyacrylonitrile,  
 polyamides, cellulose - 2 1/2 - acetate, cellu-  
 lose triacetate and especially polyesters, such  
 as polyethylene glycol terephthalate. There are  
 35 obtained, when following the usual dyeing and  
 printing processes, deep yellow, yellow-brown,  
 orange and red dyeings and prints which have  
 excellent fastness properties, particularly excel-  
 lent light and sublimation fastness. The orange  
 40 dyestuff of the present invention, having the  
 formula



- possesses particularly valuable properties. In  
 addition to its excellent light fastness, excellent  
 45 sublimation or thermofixing properties, it has  
 a very good synthesis capacity and a great  
 coloring power.

- The dyeing of synthetic hydrophobic  
 materials with the dyestuffs of the present in-  
 50 vention may be carried out from an aqueous  
 suspension including, if necessary, the pre-  
 sence of a carrier, at a temperature between  
 80 and 140° C. or by use of the so-called  
 thermofixing process at a temperature of about  
 55 180 to 230° C. Printing of these materials  
 may be carried out in such a manner that the  
 goods printed with the instant dyestuffs, if  
 necessary in the presence of a carrier, are

treated with steam at a temperature between  
 about 80 and 140° C. or are treated in accord-  
 60 ance with the so-called thermofixing process  
 at a temperature of about 180 to 230° C.

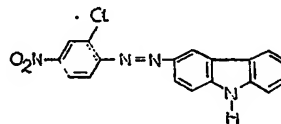
The dyestuffs of the present invention are  
 equally adapted for the dyeing of the before-  
 mentioned hydrophobic materials in organic  
 65 solvents and for the dyeing en masse.

The following examples are for the pur-  
 pose of illustrating the present invention.

#### EXAMPLE 1.

(a) In 150 parts by weight glacial acetic  
 70 acid there are diazotized 17.2 parts by weight  
 2 - chloro - 4 - nitroaniline with 34.2 parts  
 by weight nitrosyl sulfuric acid (41.3%). The  
 clear diazo solution is then allowed to run  
 75 into a solution of 18.4 parts by weight car-  
 bazole in 100 parts by weight dimethylform-  
 amide. During coupling, the temperature is  
 maintained at 10 to 15° C. by exterior cooling.  
 Following coupling, the dyestuff is recovered,  
 80 afterwashed with methanol and dried. It is  
 an orange powder and dissolves in concentrated  
 sulfuric acid to produce a red-violet colour  
 which, upon standing, turns red.

(b) Into 2000 parts by weight water, there  
 is introduced 1 part by weight of the dyestuff  
 85 of Example 1 (a) having the formula:



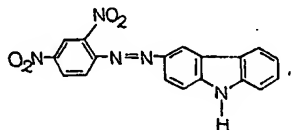
This mixture is standardized with acetic acid  
 to a pH value of 5—6 and mixed with 4 parts  
 by weight ammonium sulfate and 2 parts by  
 weight of a commercial dispersing agent which  
 90 is a naphthalene sulfonic acid-formaldehyde  
 condensate. Into the resulting dyebath, there  
 are introduced 100 parts by weight of a poly-  
 ethylene glycol terephthalate polyester fabric  
 95 and dyeing proceeds for 1 1/2 hours at 120  
 to 130° C. After washing, reductive after-  
 treatment with a 0.2% alkaline sodium di-  
 thionite solution for 15 minutes at 60—70° C.,  
 washing and drying, there is obtained a deep,  
 100 orange dyeing having very good fastness pro-  
 perties, particularly high light fastness.

#### EXAMPLE 2.

(a) Following the procedure described in  
 Example 1(a), 18.3 parts by weight of 2,4-  
 105 dinitroaniline are diazotized and then coupled  
 with 18.4 parts by weight of carbazole. After  
 stirring for 1 hour, the reaction solution is  
 mixed with 60 parts by weight anhydrous  
 sodium acetate and agitated overnight at  
 110 10—15° C. The resulting dyestuff is then fil-  
 tered with suction, washed with methanol, sub-  
 sequently washed with water and then dried.  
 It is a dark red powder which dissolves to

produce a red-violet color in concentrated sulfuric acid.

(b) Into a printing paste which contains 45 parts by weight carob bean flour, 6 parts by weight of the sodium salt of 3-nitrobenzenesulfonic acid and 3 parts by weight of citric acid per 1000 parts by weight of paste, there is incorporated in finely divided form, 30 parts by weight of the dyestuff of Example 2(a) having the formula:



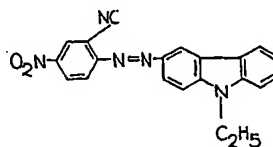
After printing with this paste, drying and fixing in the thermofixing frame for 45 seconds at 215° C., washing and finishing as described in Example 1(b), there is obtained a reddish-orange print of very good fastness properties. The same dyestuff yields an orange print of very good coloristic properties in the printing of triacetate fabric when it is used in the form of the above printing paste and the printed fabric, after drying, is steamed for 10 minutes at 1.5 atmospheres gauge pressure, washed, soaped, again washed and dried.

#### EXAMPLE 3.

(a) Employing the procedure of Example 1, 16.4 parts by weight of 2 - cyano - 4 - nitroaniline are diazotized, coupled with 21.4 parts by weight N - ethylcarbazole and isolated. The resulting dyestuff is a dark red powder which yields a blue color upon dissolving in concentrated sulfuric acid.

(b) A fabric of polyethylene glycol terephthalate is padded at 30° C. with a bath which contains 30 parts by weight of the finely

divided dyestuff of Example 3(a) having the formula:



1.0 parts by weight polyacrylamide having a K value of 120, 0.5 parts by weight of a polyglycol ether of oleyl alcohol and 968.5 parts by weight of water. After drying, fixing is carried out for 60 seconds at 210° C. in the thermofixing frame. After a subsequent washing and finishing as described in Example 1(b), there is obtained a red dyeing of excellent fastness properties.

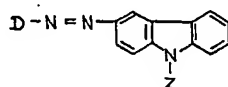
#### EXAMPLE 4.

A solution of 2 parts by weight of the dyestuff of Example 3(a) in 1500 parts by weight of tetrachloroethylene is employed in the treatment of 100 parts by weight polyester material for 30 minutes at 121° C. The treated material is washed with warm and cold tetrachloroethylene and a full, red dyeing of very good coloristic properties is obtained.

Equally good red dyeings are obtained if the polyester material of the preceding paragraph is replaced by 100 parts by weight cellulose triacetate or cellulose - 2 1/2 - acetate and dyeing is carried out for 45 minutes at 110° C. or for 45 minutes at 80° C.

The following tabulation presents further dyestuffs of the present invention which are prepared by the procedures described in Examples 1—3. When treating polyester materials with these dyes, there is obtained yellow, yellow-brown, orange and red dyeings or printings having very good fastness properties.

General formula:



No.	D	Z	No.	D	Z
1		-H	9		-H
2		-H	10		-H
3		-H	11		-H
4		-H	12		-H
5		-H	13		-H
6		-H	14		-H
7		-H	15		-CH <sub>2</sub> -CH <sub>3</sub>
8		-H	16		-CH <sub>2</sub> -CH <sub>3</sub>

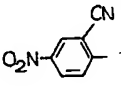
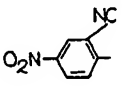
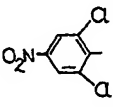
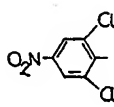
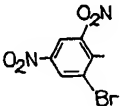
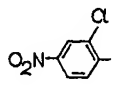
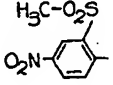
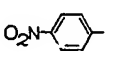
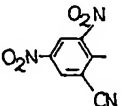
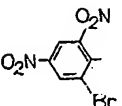
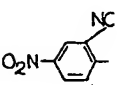
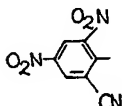
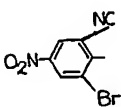
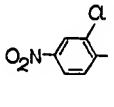
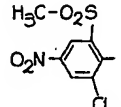
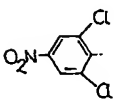
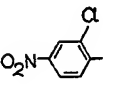
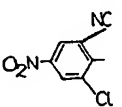
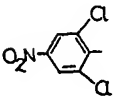
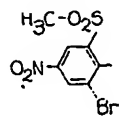
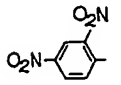
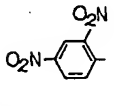
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No.	D	Z	No.	D	Z
17		-CH <sub>2</sub> -CH <sub>3</sub>	28		"
18		"	29		"
19		"	30		"
20		"	31		-H
21		"	32		-CH <sub>2</sub> -CH <sub>3</sub>
22		"	33		-H
23		"	34		-H
24		"	35		-CH <sub>2</sub> -CH <sub>3</sub>
25		"	36		"
26		"	37		-H
27		-CH <sub>2</sub> -CH <sub>3</sub>	38		-CH <sub>2</sub> -CH <sub>3</sub>

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No.	D	Z	No.	D	Z
39		-H	50		-H
40		-CH2-CH3	51		-CH2-CH3
41		-H	52		-H
42		-CH2-CH3	53		-H
43		-H	54		-CH2-CH3
44		-H	55		..
45		-CH2-CH3	56		-H
46		-H	57		-H
47		-H	58		-H
48		-H	59		-CH3
49		-H	60		..

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No.	D	Z	No.	D	Z
61		"	72		$-\text{CH}_2-\text{CH}_2-\text{CN}$
62		"	73		"
63		"	74		"
64		$-\text{CH}=\text{CH}_2$	75		$-\text{CH}_2-\text{CH}_2-\text{CH}_3$
65		"	76		"
66		$-\text{CH}=\text{CH}-\text{CH}_3$	77		"
67		"	78		$-\text{CH}(\text{CH}_3)_2$
68		"	79		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
69		$-\text{CH}=\text{CH}-\text{CH}_2-\text{Cl}$	80		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
70		$-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_3$	81		"
71		$-\text{CH}_2-\text{CH}_2-\text{CN}$	82		$-\text{C}(\text{CH}_3)_3$

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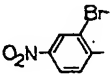
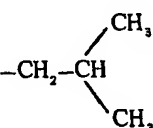
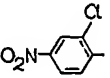
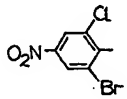
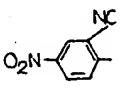
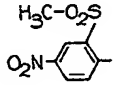
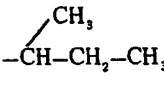
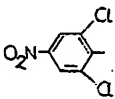
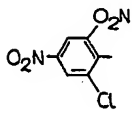
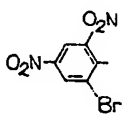
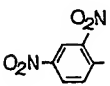
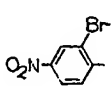
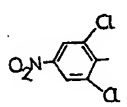
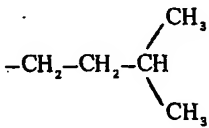

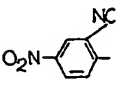


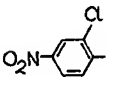
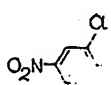

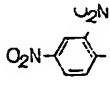
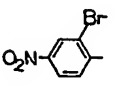
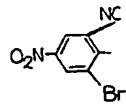
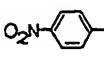
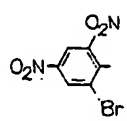
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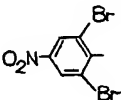
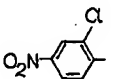
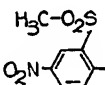
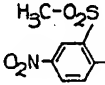
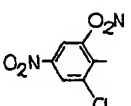
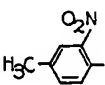
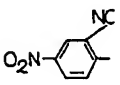
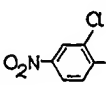


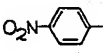
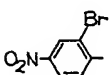
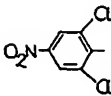
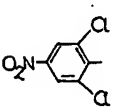




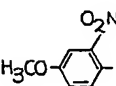


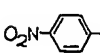
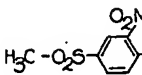

D

Z

83			94		$-\text{CH}_2-\text{CH}_2-\text{OH}$
84		..	95		..
85			96		..
86		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	97		..
87		..	98		$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$
88			99		..
89		$-(\text{CH}_2)_5-\text{CH}_3(n)$	100		$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-\text{O}-$ 
90		$-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$	101		$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-\text{O}-$ 
91	..	..	102		$-\text{CH}_2-\text{CH}_2-\text{OCH}_3$
92		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}(\text{C}_2\text{H}_5)_2$	103		..
93		..	104		..

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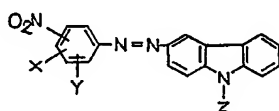
No.	D	Z	No.	D	Z
105		$-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}_2\text{H}_5$	115		$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_3$
106		„	116		„
107		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	117		$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_3$
108		„	118		$-\text{C}_6\text{H}_5$
109			119		„
110		„	120		„
111			121		
112		$-\text{CH}_2-\text{C}_6\text{H}_5$	122		
113		„	123		$-\text{C}_6\text{H}_4-\text{CH}_3$
114		„	124		„

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No.	D	Z
125		"
126		
127		
128		
129		
130		
131		

## WHAT WE CLAIM IS:—

1. Monoazo dyestuffs of the formula:



- 5 wherein X and Y are each hydrogen; halogen; cyano; nitro; or alkyl, alkylsulfonyl or alkoxy having 1 to 6 carbon atoms; and Z is hydrogen; alkyl or alkenyl having 1 to 6 carbon atoms and optionally substituted by cyano, hydroxy, acetoxy, alkoxy having 1 to 4 carbon atoms, phenoxy, phenoxyacetoxy, monoalkyl-  
 10 amine having 1 to 4 carbon atoms or dialkyl-amino having 1 to 4 carbon atoms in each alkyl moiety; phenalkyl having 1 to 2 carbon atoms in its alkyl moiety; cycloalkyl having 3 to 6 carbon atoms optionally substituted with cyano or alkyl or alkoxy having 1 to 4 carbon atoms;

or phenyl optionally substituted by cyano, or alkyl or alkoxy having 1 to 4 carbon atoms.

2. A monoazo dyestuff according to claim 1 wherein X and Y are chlorine and Z is hydrogen.

3. A monoazo dyestuff according to claim 1 wherein X is nitro and Y and Z are hydrogen.

4. A monoazo dyestuff according to claim 1 wherein X is cyano, Y is hydrogen and Z is ethyl.

5. Monoazo dyestuffs of the general formula of claim 1, as hereinbefore specifically exemplified or tabulated.

6. Synthetic, hydrophobic materials whenever dyed using a dyestuff according to any of claims 1 to 5.

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